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# Hibridon: a Program Suite for Time-Independent Non-Reactive Quantum Scattering Calculations

M. H. Alexander<sup>a</sup>, P. J. Dagdigian<sup>b</sup>, H.-J. Werner<sup>c</sup>, J. Kłos<sup>1a</sup>, B. Desrousseaux<sup>d</sup>, G. Raffy<sup>d</sup>, F. Lique<sup>d</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742 USA

<sup>b</sup>Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218 USA

<sup>c</sup>Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

<sup>d</sup>Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France

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## Abstract

Hibridon is a program package to solve the close-coupled equations which occur in the time independent quantum treatment of inelastic atomic and molecular collisions. Gas-phase scattering, photodissociation, collisions of atoms and/or molecules with flat surfaces, and bound states of weakly-bound complexes can be treated. From calculation of the  $S$  matrix, integral and differential cross sections, stereodynamic (alignment and steric asymmetry) cross sections, as well as more specialized quantities, such as transport and tensor cross sections and cross sections between hyperfine levels, and photodissociation amplitudes can be obtained. The program is capable of treating closed-shell systems where the nuclear motion takes place on a single Born-Oppenheimer potential as well as open-shell systems for which the nuclear motion can evolve on several coupled electronic (Born-Oppenheimer) potentials.

### Program Summary

*Program Title:* Hibridon

*CPC Library link to program files:* <https://doi.org/10.17632/sk9zcvz8vs.1>

*Developer's repository link:* [10.5281/zenodo.7551616](https://zenodo.org/record/7551616)

*Licensing provisions:* GPLv3

*Programming language:* Fortran 90

*External routines/libraries:* LAPACK, BLAS

*Nature of problem:* Solution of the time-independent Schrödinger equation for the inelastic scattering of atoms and molecules, for the photodissociation of molecules, and for the ro-vibrational motion of weakly bound molecular complexes.

*Solution method:* The scattering wavefunction is expanded in a set of internal states of the system, constructed as direct products of the internal states of one (or both) fragments and angular functions which describe the rotation of one collision partner about the other. The Schrödinger equation for the nuclear motion is solved by determining the expansion coefficients as a function of the interparticle separation starting from the short-range classically forbidden region outwards to the asymptotic region. The  $S$  matrix is given by the asymptotic behavior of the wavefunction. Integral and differential cross sections, as well as other scattering and photodissociation quantities are calculated from the  $S$  matrix.

*Keywords:* Inelastic atomic and molecular collisions and/or molecular photodissociation, time-independent quantum scattering calculations,  $S$  matrix, cross sections, weakly-bound complexes

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<sup>1</sup>Current affiliation: Joint Quantum Institute, Department of Physics, University of Maryland, College Park, MD 20742

*Email addresses:* mha@umd.edu (M. H. Alexander), pjdagdigian@jhu.edu (P. J. Dagdigian), werner@theochem.uni-stuttgart.de (H.-J. Werner), jklos@umd.edu (J. Kłos), benjamin.desrousseaux@univ-rennes1.fr (B. Desrousseaux), guillaume.raffy@univ-rennes1.fr (G. Raffy), francois.lique@univ-rennes1.fr (F. Lique)

## 1. Introduction

Molecular collisions are an important mechanism by which energy is exchanged between the translational and internal molecular degrees of freedom. This process governs the equilibration of a gaseous system toward thermodynamic equilibrium. In the low-pressure interstellar medium, collisions in combination with radiative processes govern the distribution of rotational populations of astrophysical molecules [1, 2].

Within the Born-Oppenheimer approximation for the separation of electronic and nuclear motion, the interaction between atomic and molecular species is governed by one (or more) electronic potential energy surfaces (PES). These PES(s) are independent of the masses and spins of the nuclei. Treatment of molecular collisions, photodissociation, and/or the bound states of molecular complexes involves solution of the quantum mechanical Schrödinger equation for the nuclear motion on this PES(s). The most rigorous approach is the time-independent close-coupling (CC) formalism, developed originally by Arthurs and Dalgarno [3] for inelastic atom-molecule scattering.

From a knowledge of the PES for a given system, the Hibridon package provides the means to solve these close-coupled equations to obtain dynamical quantities of interest. Section 2 provides a brief description of the underlying scattering theory and the subsequent calculation of cross sections. Sections 3 and 4 describe the treatment of bound states and photodissociation, respectively. Section 5 discusses in more detail the types of collision systems that can be handled by Hibridon. Sections 6–9 provide information on the installation and use of Hibridon.

The name Hibridon arises from the use of the hybrid integration scheme described in more detail below. The original program package was first referenced in 1987 [4]. Over the years, many enhancements have been added, including the addition of a number of basis routines. In addition to the determination of integral and differential cross sections, the code treats photodissociation and allows the calculation of tensor, transport, and pressure broadening cross sections. Cross sections calculated by Hibridon have been successfully compared with those obtained using the widely employed Molscat program [5]. This includes calculations on the CO–He and CO–H<sub>2</sub> systems for which the cross sections calculations by the two program suites differ by ~ 1%. A recent check in Google Scholar revealed that since its introduction Hibridon has been referenced in over 350 scientific publications and in 10 review articles.

The Hibridon package has been utilized in the past successfully to guide and interpret experimental results. For example, in the case of the open-shell molecule of <sup>2</sup>Π character, Nizamov *et al.* [6] studied experimentally and theoretically using Hibridon collisions of CN(A<sup>2</sup>Π) radical with He. Later, de Lange *et al.* [7] used Hibridon to compute Λ-doublet propensities and steric asymmetry cross sections that compared well to the experiment.

## 2. Scattering Theory

In the close-coupled treatment the overall scattering wavefunction is expanded as a direct product of (ideally) a complete set of wavefunctions describing the internal states of one (or both) collision partners and angular functions describing the rotation of the collision partners about each other. These angular functions are vector coupled to give eigenfunctions of the total angular momentum  $J$ . The orthogonal set of these product states can be designated as a column vector  $\phi(\hat{\mathbf{R}}, \mathbf{r})$ , where  $\mathbf{r}$  denotes the internal coordinates and  $\hat{\mathbf{R}} = (\theta, \phi)$  describes the orientation of  $R$ , the separation of the centers of mass of the collision partners.

Following Arthurs and Dalgarno [3], we express the internal coordinates of the complex in the space frame. The full scattering wavefunction can be written as

$$\Phi(\mathbf{R}, \mathbf{r}) = R^{-1} \sum \mathbf{F}(R)\phi(\hat{\mathbf{R}}, \mathbf{r}). \quad (1)$$

Each column of the  $\mathbf{F}(R)$  matrix defines the expansion coefficients for collisions in which the collision partners start out in the particular initial state whose index is that of the selected column.

Substitution of Eq. 1 into the Schrödinger equation, premultiplication by one of the internal states, and integration over  $\mathbf{r}$  gives rise to a set of coupled ordinary differential equations for the expansion coefficients  $\mathbf{F}(R)$ . These coupled second-order ordinary differential equations in  $R$  (the so-called "closed-coupled" equations) can be written succinctly as the matrix equation

$$\left[ \mathbf{I} \frac{d^2}{dR^2} + \mathbf{W}(R) \right] \mathbf{F}(R) = 0. \quad (2)$$

Here  $\mathbf{I}$  denotes the identity matrix and the matrix  $\mathbf{W}(R)$  is given by

$$\mathbf{W}(R) = \mathbf{k}^2 - \mathbf{I}^2 - \frac{2\mu}{\hbar^2} \mathbf{V}(R), \quad (3)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $\mu$  is the reduced mass of the collision system, and  $\mathbf{k}$  and  $\mathbf{I}$  are the (diagonal) matrices of the wavevector and the relative orbital momentum of the collision partners. Here, also  $\mathbf{V}(R)$  is the total quasi-adiabatic potential matrix, which for the case of closed-shell system described by a single Born-Oppenheimer potential operator is equivalent to the adiabatic potential. The diagonal matrix elements of  $\mathbf{k}^2$  and  $\mathbf{I}^2$  matrices are

$$(k)_{ii}^2 = \frac{2m}{\hbar^2} (E - \varepsilon_i), \quad (4)$$

where  $E$  is the total energy,  $\varepsilon_i$  is the internal energy of the  $i^{\text{th}}$  channel and

$$(I)_{ii}^2 = \frac{\hbar^2}{2mR^2} l_i(l_i + 1). \quad (5)$$

Here,  $l_i$  is the relative orbital angular momentum of the  $i^{\text{th}}$  channel. Note that we assume that the potential matrix vanishes as the particles separate, namely

$$\lim_{R \rightarrow \infty} \mathbf{V}(R) = 0. \quad (6)$$

Because of the importance of inelastic collisions in a wide variety of physical phenomena, a number of techniques have been developed to solve the close-coupled equations (Eq. 2) [8]. The Hibridon package incorporates a hybrid integration scheme [9]. At short range (small  $R$ ) a solution-following method [10] is used, based on the log-derivative algorithm of Johnson [11], as modified by Manolopoulos [12]. In the Hibridon package, this propagator is designated LOGD. At long range, a potential-following method [10] is used, based on the linear-reference potential algorithm of Gordon [13, 14], as modified by Alexander and Manolopoulos [9, 15]. This propagator is designated AIRY. The Hibridon code combines these two propagators (LOGD and AIRY), which are both numerically stable and computationally fast. The numerical stability is achieved by propagation of the logarithmic derivative of the solution matrix  $\mathbf{F}(R)$ , namely

$$\mathbf{Y}(R) = \mathbf{F}'(R) \mathbf{F}(R)^{-1}, \quad (7)$$

rather than the solution matrix  $\mathbf{F}(R)$  itself. The speed arises from the ability of the AIRY propagator to take increasingly larger steps at long range. A demonstration of this is the study of long-range charge-dipole scattering, where the potential varies at long range as  $R^{-2}$  [15].

Initially, at a value of  $R$  ( $R = R_{\text{start}}$ ) which lies well within the innermost classical turning point, we assume that in a locally adiabatic basis, defined by diagonalization of the matrix  $\mathbf{W}(R = R_{\text{start}})$  of Eq. 3, the matrix of solutions  $\mathbf{F}(R)$  is an increasing exponential in all channels. Note that the eigenvectors of  $\mathbf{W}(R_{\text{start}})$  are all negative. As a consequence, in this locally adiabatic basis the log-derivative matrix is a diagonal matrix with elements equal to the square roots of the negative of these eigenvectors. The initial log-derivative matrix  $\mathbf{Y}(R_{\text{start}})$  is obtained by a back orthogonal transformation to the asymptotic basis.

The log-derivative matrix is propagated from  $R_{\text{start}}$  out to a value of  $R$  ( $R = R_{\text{end}}$ ) which is so large that the potential  $\mathbf{V}(R_{\text{end}})$  is negligible compared to the wavevectors  $\mathbf{k}^2$ . At that point, all the scattering information can be obtained by matching the numerically propagated  $\mathbf{Y}(R_{\text{end}})$  to an asymptotic form imposed by the scattering boundary conditions. This latter can be obtained from the asymptotic form of the solution matrix  $\mathbf{F}(R_{\text{end}})$  and its derivative, which correspond to the imposition of the usual scattering boundary conditions. For  $\mathbf{F}(R)$  we have

$$\lim_{R \rightarrow \infty} \mathbf{F}(R) = \hat{\mathbf{h}}^{(2)}(R) - \mathbf{S} \hat{\mathbf{h}}^{(1)}(R). \quad (8)$$

Here, we have introduced the scattering matrix  $\mathbf{S}$ . It is convenient to define also the transition matrix  $\mathbf{T} = \mathbf{I} - \mathbf{S}$ .

In Eq. 8  $\hat{\mathbf{h}}^{(1)}$  and  $\hat{\mathbf{h}}^{(2)}$  are diagonal matrices with elements

$$\hat{h}_{ii}^{(1,2)}(R) = k_i^{-1/2} h_i^{(1,2)}(k_i R), \quad (9)$$

and  $h_l^{(1,2)}$  are complex spherical Hankel functions [16]

$$h_l^{(1,2)}(x) = j_l(x) \pm iy_l(x). \quad (10)$$

In Eq. 10, the plus and minus signs correspond to the Hankel functions of the first and second kind, respectively. The functions  $j_l(x)$  and  $y_l(x)$  are spherical Bessel functions and are defined in terms of Bessel functions of half-integral order as follows [16]

$$j_n(x) = (\pi/2x)^{1/2} J_{n+\frac{1}{2}}(x), \quad (11)$$

$$k_n(x) = (\pi/2x)^{1/2} Y_{n+\frac{1}{2}}(x). \quad (12)$$

The spherical Hankel functions with a superscript carat [Eq. 8] are denoted Ricatti-Hankel functions.[16] To obtain the asymptotic expression for  $\mathbf{Y}(R)$  we also need the asymptotic expression for the first derivative of  $\mathbf{F}(\mathbf{R})$ . This can be easily obtained from Eqs. 8–10. From the  $S$  and  $T$  matrices, cross sections can be computed, as will be described below.

### 2.1. Integral Cross Sections

The integral cross section (which can be calculated with the command INTCRS) for transition from initial level  $i$  to final level  $f$ , with rotational angular momenta  $j$  and  $j'$ , respectively, in the collision of a molecule with a structureless target is given by

$$\sigma_{i \rightarrow f} = \frac{\pi}{[j] k_i^2} \sum_{Jpl'} (2J+1) |T_{il,fl'}^{J,p}|^2, \quad (13)$$

where  $[x] = 2x+1$ ,  $k_i$  is the wavevector of the initial level,  $p$  is the parity, which equals  $\pm 1$ , and  $l$  and  $l'$  are the initial and final orbital angular momenta, respectively. The sums run over all values of the total angular momentum  $J$  for which the  $S$ -matrix elements differ from a magnitude of unity. The last term in Eq. 13 is an element of the  $T$  matrix. The total angular momentum  $J$  and parity  $p$  are conserved in the collision. As a consequence the individual terms in the sum in Eq. 13 can be calculated separately for each  $(J, p)$  partial wave.

In the case of a collision between two particles both with internal structure, the cross section for a state-to-state transition  $j_1 j_2 \rightarrow j'_1 j'_2$  is given by

$$\sigma_{i \rightarrow f} = \frac{\pi}{[j_1][j_2] k_i^2} \sum_{Jp j_{12} j'_{12} l'} (2J+1) |T_{ij_{12}l, f j'_{12}l'}^{J,p}|^2, \quad (14)$$

where the intermediate angular momenta  $j_{12}$  and  $j'_{12}$  equal the vector sums  $j_1 + j_2$  and  $j'_1 + j'_2$ , respectively.

Note that with flag CSFLAG set .TRUE. one can use the centrifugal decoupling (or coupled-states, CS) scheme [17, 18] to simplify (but at a potential loss in accuracy) calculations of integral cross sections.

### 2.2. Differential Cross Sections

Differential cross sections [19], and/or stereodynamic quantities (diagonal and off-diagonal alignment moments, [20, 21] steric asymmetry cross sections [22] and  $m$ -dependent cross sections) can be calculated with the Hibridon package. Collisions with both structureless targets and targets with internal structure can be treated. Differential cross sections are obtained from the scattering amplitudes  $f$  that can be computed from the  $S$  matrix (or from the  $T$  matrix). The stereodynamics quantities that can be computed are diagonal quadrupole and hexadecapole alignment moments denoted  $A_0^{(2)}$  and  $A_0^{(4)}$ , respectively, defined as in Greene *et al.* [20]. The off-diagonal alignment moment  $A_2^{(2+)}$  is also computed following Zare *et al.* [23] and Kay *et al.* [24] as:

$$A_2^{(2+)}(j) = 2^{-1/2} [\mathcal{A}_2^{(2)}(j) + \mathcal{A}_{-2}^{(2)}(j)], \quad (15)$$

where

$$\mathcal{A}_q^{(k)}(j) = \frac{(-1)^q c(k)}{\langle jm | \mathbf{J}^2 | jm \rangle^{k/2}} \frac{(j \parallel \mathbf{J}^{(k)} \parallel j)}{[k]} \rho_{-q}^{(k)}(j). \quad (16)$$

The spherical tensor components of the density matrix are defined as

$$\rho_q^{(k)}(J) = \sum_{mm'} (-1)^{j-m'} [k] \begin{pmatrix} j & k & j' \\ -m & -q & m' \end{pmatrix} \rho_{m'm}. \quad (17)$$

In a collision experiment, the transition out of initial rotational level  $j$  into final rotational level  $j'$  at scattering angle  $\theta$  is fully described by the  $m$ -resolved complex scattering amplitudes  $f_{jm \rightarrow j'm'}(\theta)$ . (We will suppress the scattering angle unless explicitly needed). In terms of these, the  $\{m, m'\}^{\text{th}}$  element of the density matrix for final rotational level  $J$  at scattering angle  $\theta$  is

$$\rho_{m'm} = \sum_{m''} f_{j''m'' \rightarrow jm'}^* f_{j''m'' \rightarrow jm} \left/ \sum_{m'', m'} |f_{j''m'' \rightarrow jm'}|^2 \right. . \quad (18)$$

The denominator is chosen so that  $\text{Tr}(\rho_{m'm}) = \sum_m \rho_{mm} = 1$ .

The differential cross section command (DIFCRS) control the calculation of the above quantities with the additional capability of printing  $m$ -dependent cross sections and steric (oriented) asymmetry cross sections [22].

### 2.3. Hyperfine cross sections

Since nuclear hyperfine splittings are usually much smaller than rotational energy spacings, it is sufficient to compute cross sections between nuclear hyperfine levels using the recoupling method [25, 26]. Here, the  $T$  matrix is obtained from the nuclear-spin-free  $T$  matrix. Hyperfine cross sections can be computed for both atom-molecule [25] and molecule-molecule [26] collisions. Hyperfine cross sections can also be calculated when both collision partners have nonzero nuclear spins, provided that one of the collision partners has no internal structure (*e.g.* an atom-molecule collision).

The hyperfine cross section command (HYPXSC) controls the calculation of cross sections for transitions between hyperfine levels.

### 2.4. Tensor cross sections

The tensor cross section of order  $K$  for a transition from state  $i$  to state  $f$  in collisions with a structureless target and for an isotropic velocity distribution is given by [27, 28, 29, 30]

$$\sigma_{i \rightarrow f}^K = \frac{\pi}{k_i^2} \sum_{JJ'l'l'} [J][J'] (-1)^{l+l'-j-j'+2J} \left\{ \begin{matrix} j & j & K \\ J & J' & l \end{matrix} \right\} \left\{ \begin{matrix} j' & j' & K \\ J & J' & l' \end{matrix} \right\} T_{ijl, f'j'l'}^J (T_{ijl, f'j'l'}^{J'})^* .$$

Here,  $\{:::\}$  is a  $6j$  symbol.[31] Several choices of the quantization axis are possible in Hibridon. Subsequently,  $m, m'$  resolved cross sections can be computed from the tensor cross sections.

The tensor cross section command (TENXSC) controls the calculation of tensor cross sections.

### 2.5. Pressure broadening cross sections

The cross section for pressure broadening of an isolated line, from an initial level  $i$  with total angular momentum  $j$  to a final level  $f$  with angular momentum  $j'$ , induced by collisions with a structureless target can be written as [32, 33]

$$\sigma_{i \rightarrow f}^K = \frac{\pi}{k_i^2} \sum_{JJ'l'l'} [J][J'] (-1)^{l-l'} \left\{ \begin{matrix} j & K & j' \\ J' & l & J \end{matrix} \right\} \left\{ \begin{matrix} j & K & j' \\ J' & l' & J \end{matrix} \right\} (\delta_{ll'} - S_{f'l', il}^{J'*}(E_{\text{tot}}) S_{f'l', il}^J(E'_{\text{tot}})) . \quad (19)$$

In Eq. 19,  $K$  is the tensor order ( $K=1$  for dipole transitions and  $K=0$  or  $2$  for Raman transitions). The first and second set of  $S$ -matrix elements in Eq. 19 are computed for the initial and final levels, respectively, in close-coupling scattering calculations at total energies  $E_{\text{tot}}$  and  $E'_{\text{tot}}$  corresponding to the same collision energy. The real and imaginary parts of the pressure broadening cross section in Eq. 19 contribute to the broadening and shifting of the line, respectively.

The command PRSBR controls calculation of pressure broadening cross sections. Note that for pressure-broadening cross sections the user should use the log-derivative propagator LOGD to solve the close-coupled equations over the full range of  $R$ .

## 2.6. Transport cross sections

Transport properties can be calculated through the use of collision integrals, which are defined as a Boltzmann average over state-dependent collision integrals [34, 35]

$$\Omega^{(n,s)}(T) = \frac{1}{q_R} \sum_j (2j+1) \exp(-\varepsilon_j/k_B T) \Omega_j^{(n,s)}(T). \quad (20)$$

Here, again,  $\varepsilon_i$  is the energy of the  $i^{\text{th}}$  rotational level,  $q_R$  is the rotational partition function, and  $k_B$  is the Boltzmann constant. The state-dependent collision integrals are defined by [34, 36]

$$\Omega_j^{(n,s)}(T) = \frac{1}{2} \left( \frac{k_B T}{2\pi\mu} \right)^{1/2} \frac{1}{k_B T^{s+2}} \int_0^\infty E^{s+1} \exp(-E/k_B T) Q_j^{(n)}(E) dE. \quad (21)$$

The state-dependent effective cross section  $Q_{ji}^{(n)}(E)$  is a sum over final levels  $j_f$  of state-to-state effective cross sections [36]

$$Q_j^{(n)}(E) = \sum_{j'} Q_{j \rightarrow j'}^{(n)}(E), \quad (22)$$

where the later quantities are weighted angle averages of the  $j \rightarrow j'$  differential cross sections:

$$Q_{j \rightarrow j'}^{(n)}(E) = \int \left( \frac{d\sigma}{d\Omega} \right)_{j \rightarrow j'} \Phi_n(E) d\hat{R}. \quad (23)$$

The weighting factors in Eq. 23 have been given previously [34]. The cross sections can be expressed as a weighted sum of several low-order Legendre moments [37] of the differential cross section. Determination of the effective cross sections  $Q_{ji}^{(1)}(E)$  are controlled by the command TRNPRT in Hibridon.

## 3. Determination of Bound States

In an entirely equivalent manner to the description of molecular collisions, one can use a close-coupled (CC) or coupled-states (CS) expansion to determine wavefunctions of bound states of weakly bound complexes. For more detail we refer the reader to an excellent review by Hutson [38]. As described above in Sec. 2, the wavefunction of the complex is similarly expanded in a complete set of internal states of the system, usually constructed as direct products of the internal states of one (or both) fragments, multiplied by angular functions which describe the rotation of one collision partner about the other. As in the earlier description of scattering we designate these internal states as  $\phi(\mathbf{r})$ , where  $\mathbf{r}$  designates the internal coordinates. Each internal state is called a channel. The full wavefunction of the complex is written as expressed in Eq. 1. The  $n^{\text{th}}$  column of the  $\mathbf{F}(R)$  matrix defines the expansion coefficients for the  $n^{\text{th}}$  bound state.

Diagonalization of the  $\mathbf{W}(R)$  matrix shown in Eq. 3 yields the diagonal matrix of adiabatic wavevectors  $\mathbf{k}(R)$ . The eigenvectors define the locally adiabatic states, which are transformations of the internal states used to expand the scattering wavefunction,  $\Phi(R, \mathbf{r})$ . If  $\mathbf{C}(R)$  designates the matrix of eigenvectors, column ordered, then the diagonal matrix of adiabatic energies, sometimes referred to as the "adiabatic bender" energies, is defined as [39]

$$\mathbf{e}(R) = \mathbf{C}(R)^T \mathbf{V}(R) \mathbf{C}(R). \quad (24)$$

### 3.1. Bound State Energies and Wavefunctions

The Hibridon package uses a variational method based on the distributed Gaussian basis approach of Hamilton and Light [40] to determine energies and wavefunctions of bound states. Each element of the solution matrix,  $F_{ij}(R)$ , is expanded in terms of a set of functions in the separation coordinate  $R$

$$F_{ij}(R) = \sum_{m=1}^M C_{mi}^{(j)} \chi_m(R). \quad (25)$$

As in any standard linear variational technique, the energy and eigenfunction of the  $n^{\text{th}}$  bound state is obtained by diagonalization of the matrix of the full Hamiltonian  $\mathbf{H}(R) = \mathbf{T}(R) + \mathbf{W}(R)$ , where  $\mathbf{T}(R)$  is a radial kinetic energy operator, in the  $\chi(R)$  basis. The dimensions of this Hamiltonian matrix are  $M \times N_{\text{ch}}$ , where  $M$  is the dimensionality of the  $\chi(R)$  basis and  $N_{\text{ch}}$  is the number of internal states (channels). In the Hibridon package, the uniformly distributed Gaussian basis suggested by Hamilton and Light [40] is used, in which

$$\chi_m(R) = e^{-\alpha(R-R_m)^2}, \quad (26)$$

where  $R_m$  is the midpoint of the the  $m^{\text{th}}$  Gaussian function. The Hibridon code will calculate bound-state energies if the flag BOUNDC is set .TRUE.

This set of  $\chi(R)$  functions is defined by several input parameters, as follows:

1. R1: smallest value of  $R_m$
2. R2: largest value of  $R_m$
3. SPAC: spacing between successive values of  $R_m$
4. C: parameter which determines the exponential scale factor of the distributed Gaussian functions, with  $\alpha = (C/\text{SPAC})^2$ .
5. EIGMIN: lower limit on the minimum allowed eigenvalue of the overlap matrix. If the minimum eigenvalue is less than this value, the parameter C should be increased.
6. DELR, HSIMP: The matrix elements of  $\mathbf{W}(R)$  are evaluated by a Simpson's rule integration extending from  $R1 - \text{DELR}$  to  $R2 + \text{DELR}$  in steps of HSIMP.

#### 4. Photodissociation

The Hibridon code can also treat photodissociation, in a time-independent manner. The homogeneous set of close-coupling scattering equations [Eq. 2] are replaced by a similar set of *inhomogeneous* equations [41, 42, 43]:

$$\left[ \mathbf{I} \frac{d^2}{dR^2} + \mathbf{W}(R) \right] \mathbf{F}(R) = \chi(R), \quad (27)$$

which are solved subject to the boundary conditions

$$\lim_{R \rightarrow 0} \mathbf{F}(R) = 0, \quad (28)$$

and

$$\lim_{R \rightarrow \infty} \mathbf{F}(R) = \mathbf{O}(R) \boldsymbol{\tau}. \quad (29)$$

Here  $\mathbf{O}(R)$  is a diagonal matrix of flux normalized outgoing wave components in each fragment channel, the elements of which are related to the outgoing Ricatti-Hankel functions defined in Eq. 10, by [42]

$$O_{ii}(R) = (\hbar k_i / m) \hat{h}_i^{(1)}(R). \quad (30)$$

The  $i^{\text{th}}$  row of the column vector  $\boldsymbol{\tau}$  gives the amplitude for dissociative excitation into internal state  $i$  of the fragments. In the case of photodissociation Eq. 29 is the analogue of Eq. 8.

Finally, in Eq. 27 the  $i^{\text{th}}$  element of the column vector  $\chi(R)$  is proportional to the vibrational wavefunction of the electronic ground state multiplied by the bound-dissociative transition dipole moment projected onto the same channel basis (indexed here by  $i$ ) used to expand the photofragment wavefunction. In the case of photodissociation, the user must provide a separate subroutine GROUND which, at each value of  $R$  returns the elements of the  $\chi$  column vector.

The Hibridon flag PHOTOF should be set .FALSE. if the standard inelastic scattering boundary conditions of Eq. 8 are assumed, but set .TRUE. if the photodissociation boundary conditions of Eq. 29 are assumed.

#### 5. Systems Handled

The subsections below list the collision systems handled by Hibridon. Note that the code can treat collisions between collision partners with many different spatial, electronic and spin symmetries. The Hamiltonian for each system is defined by the spectroscopic parameters employed. This is explained in more detail in the Github Hibridon repository in the help section related to the basis subroutines. [44].

\*These bases are covered and validated by automatic testing (see Section 7)



### 5.1. Basis 1: (ba1sg)\*

This subroutine treats the collision of a linear molecule in a  $^1\Sigma$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [45].

### 5.2. Basis 2: (ba2sg)\*

This subroutine treats the collision of an open-shell linear molecule in a  $^2\Sigma$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [46].

### 5.3. Basis 3: (ba2pi)\*

This subroutine treats the collision of an open-shell linear molecule in a  $^2\Pi$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [47, 48, 49].

### 5.4. Basis 4: (basgpi)

This subroutine treats the collisional mixing of a  $^2\Pi$  state, in an intermediate coupling basis, and a  $^2\Sigma$  electronic state of a linear molecule induced by a structureless atom/ion in a  $^1S$  electronic state [50, 51].

### 5.5. Basis 5: (bapi)

This subroutine treats the collision of an open-shell linear molecule in a  $^1\Pi$  electronic state in a Hund's case (a) basis or a  $^2,3\Pi$  state in an intermediate coupling basis with a structureless atom/ion in a  $^1S$  electronic state. Stark mixing of the  $\Lambda$ -doublet levels by an external electric field can also be included [47, 48, 49, 52].

### 5.6. Basis 6: (bastp)\*

This subroutine treats the collision of a closed-shell symmetric top molecule possessing inversion doubling (e.g.  $\text{NH}_3$ ) with a structureless atom/ion in a  $^1S$  electronic state [53, 54].

### 5.7. Basis 7: (ba13p)\*

This subroutine treats the collision of an atom in a  $^1P$  and/or a  $^3P$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [55, 56, 57].

### 5.8. Basis 8: (ba2mol)

This subroutine treats the collision between two closed-shell identical heteronuclear diatomic molecules in  $^1\Sigma$  electronic states [58, 59, 60]. This legacy subroutine was designed for HF–HF collisions and is not currently working.

### 5.9. Basis 9: (bastpln)

\* This subroutine treats the collision of a rigid closed-shell symmetric top molecule, whose rotational levels show inversion doubling, with a closed-shell diatomic molecule in a  $^1\Sigma$  electronic state [61].

### 5.10. Basis 10: (ba22p)

This subroutine treats the collision of an atom in a  $^2P$  electronic state with an atom in a  $^2S$  electronic state [62].

### 5.11. Basis 11: (ba1del)

This subroutine treats the collision a linear molecule in a  $^1\Delta$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [63].

### 5.12. Basis 12: (bah2p)\*

This subroutine treats the collision of an open-shell atom in a  $^2P$  electronic state with a homonuclear diatomic molecule in a  $^1\Sigma_g^+$  electronic state [64].

### 5.13. Basis 13: (bah3p)\*

This subroutine treats the collision of an open-shell atom in a  $^3P$  electronic state with a homonuclear diatomic molecule in a  $^1\Sigma_g^+$  electronic state [65].

### 5.14. Basis 14: (ba2del)

This subroutine treats the collision a linear molecule in a  $^2\Delta$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [66].

### 5.15. Basis 15: (badiat2p)

This subroutine treats the collision of an open-shell atom in a  $^2P$  electronic state with a heteronuclear diatomic molecule in a  $^1\Sigma^+$  electronic state. This subroutine has not been tested in scattering calculations.

### 5.16. Basis 16: (baastp)\*

This subroutine treats the collision of a closed-shell asymmetric top molecule with a structureless atom/ion in a  $^1S$  electronic state [67].

### 5.17. Basis 17: (bach2x)\*

This subroutine treats the collision of a  $\text{CH}_2(\tilde{X}^3B_1)$  in the  $(0, v_2, 0)$  bender vibrational level with a structureless atom/ion in a  $^1S$  electronic state [68, 69]. The  $\text{CH}_2(\tilde{X}^3B_1)$  molecule has a low barrier to linearity, and its rotational energies are not at all well described by the standard rotational energy formulas. Hence, the rovibrational energies were taken from Morse oscillator-rotating bender internal dynamics (MORBID) calculations by Jensen, Bunker, and so-workers [70, 71].

### 5.18. Basis 18: (bastp1)\*

This subroutine treats the collision of a closed-shell symmetric top molecule with no inversion doubling and a spherically symmetric atom/ion in a  $^1S$  electronic state [53, 72]. This version has the capability of setting up calculations for all 3 nuclear spin modifications of  $\text{CD}_3$ .

### 5.19. Basis 19: (basgpi1)

This subroutine treats the collisional mixing of  $^2\Pi$  and  $^2\Sigma$  electronic states of a linear molecule induced by a structureless atom/ion in a  $^1S$  electronic state [50, 51]. It is assumed that there is no isolated-molecule mixing of the  $\Sigma$  and  $\Pi$  states.

### 5.20. Basis 20: (ba2pi1sg)\*

This subroutine treats the collision of an open-shell linear molecule in a  $^2\Pi$  electronic state with a diatomic molecule in a  $^1\Sigma$  electronic state [73].

### 5.21. Basis 21: (bastp1sg)\*

This subroutine treats the collision between a closed-shell symmetric top molecule and a diatomic molecule in a  $^1\Sigma$  electronic state [61, 74]. A coupled representation of the PES is employed. Unlike basis 9, the symmetric top is assumed here to have no inversion doubling.

### 5.22. Basis 22: (ba1d3p)

This subroutine treats the collision of an atom in a  $^1D$  and/or  $^3P$  electronic state with a structureless atom/ion in a  $^1S$  electronic state [75]. Both electrostatic and spin-orbit coupling of the atomic states is considered.

### 5.23. Basis 23: (ba3p2s)

This subroutine treats the collision of an atom in a  $^3P$  electronic state with another atom in a  $^2S$  electronic state [76]. Both electrostatic and spin-orbit interactions are included.

#### 5.24. Basis 24: (basptp)\*

This subroutine treats the collision of a closed-shell spherical top molecule with a structureless atom/ion in a  $^1S$  electronic state [77].

#### 5.25. Basis 25: (ba1sg1sg)\*

This subroutine treats the collision of a closed-shell diatomic molecule in  $^1\Sigma$  electronic state with a different closed-shell diatomic molecule in a  $^1\Sigma$  electronic state [58]. The second molecule can be homonuclear.

#### 5.26. Basis 26: (ba2sg1sg)\*

This subroutine treats the collision of a diatomic molecule in  $^2\Sigma$  electronic state with a closed-shell diatomic molecule in a  $^1\Sigma$  electronic state [78]. The second molecule can be homonuclear.

#### 5.27. Basis 27: (baastp1)

This subroutine treats the collision of a closed-shell asymmetric top molecule possessing  $C_{2v}$  symmetry and having the quantization axis along the  $C_2$  axis with a structureless atom/ion in a  $^1S$  electronic state. The body-frame  $z$ -axis of the system is taken to lie along the  $C_2$  symmetry axis of the molecule, following Green's convention [79, 80].

#### 5.28. Basis 28: (ba3sg1sg)\*

This subroutine treats the collision of a diatomic molecule in  $^3\Sigma^-$  electronic state with a closed-shell diatomic molecule in a  $^1\Sigma$  electronic state [81]. The second molecule can be homonuclear.

#### 5.29. Basis 29: (baastp2)

This subroutine treats the collision of a chiral asymmetric top molecule, i.e. a molecule having no symmetry elements, with a structureless atom/ion in a  $^1S$  electronic state [82].

#### 5.30. Basis 30: (baastp3)

This subroutine treats the collision of an asymmetric top molecule possessing either  $C_{2v}$  or  $C_s$  symmetry with a linear molecule in a  $^1\Sigma$  electronic state. For a molecule with the  $C_{2v}$  symmetry, the body-frame  $z$ -axis lies along the  $C_2$  symmetry axis of the molecule, following Green's convention [79, 80]. For a molecule with only  $C_s$  symmetry, the molecule-frame  $z$ -axis lies along the inertial  $A$ -axis of the asymmetric top [83].

#### 5.31. Basis 99 and higher (user-defined basis) (bausr)\*

Basis 99 treats the collision of a molecule with a structureless particle, while basis 100 treats the collision of a molecule with a particle having internal structure. The user must provide the angular coupling potential and a calculation of the energy levels.

## 6. Main Parameters

### 6.1. Integral cross sections: INTCRS command

The command INTCRS allows you to determine (and print out) integral cross sections (in units of  $\text{\AA}^2$ ) from a previously calculated set of  $S$  matrices which have been written to file {jobname}n.smt. The command line syntax is

```
INTCRS, {jobname}, ienerg
```

where

- {jobname}: the jobname under which the  $S$  matrices have been stored as {jobname}n.smt. Here  $n$  denotes the value of the parameter `ienerg` (see below).  $S$ -matrix (.smt) files can be generated by setting the flag `WRSMAT = .TRUE.`. The default value of {jobname} is the value of the jobname you have set with the command `JOB = {jobname}`

Note that for full close-coupling determinations of integral cross sections the previous calculations of the  $S$  matrices must have been done for both values of the parity index JLPAR (this is ensured by setting JLPAR = 0; see the JLPAR frame for more information)

If no value has been set, the default value of {jobname} is JOB

- **ienerg**: The cardinal value of the energy for which the integral cross sections are to be computed. i.e. if **ienerg** = 2, then the second energy  $S$  matrix file {jobname}2.smt is used. The default value of **ienerg** is 1

The calculated integral cross sections are printed out in file {jobname}{ienerg}.xsc

## 6.2. Differential cross sections: DIFCRS command

The command DIFCRS allows you to compute from previously determined  $S$ -matrix elements (moments are dimensionless; cross sections are in  $\text{\AA}^2/\text{sr}$ ):

1. differential cross sections
2. diagonal quadrupole and octupole alignment moments
3. off-diagonal alignment moments
4.  $m$ -dependent cross sections
5. steric (oriented) cross sections

DIFCRS, {jobname}, j1, in1, j2, in2, ang1, ang2, dang, ienerg, jtotend, ipr, mflag, stflag, alpha, beta

where {jobname} designates the jobname under which the  $S$  matrices have been stored {jobname}n.smt. Here  $n$  denotes the value of the parameter **ienerg** (see below). These  $S$  matrices must have been previously generated using

- JLPAR = 0 (this generates  $S$  matrices for both parities)
- JTOT1 = 1 (ensuring the determination of  $S$  matrices at every partial wave)
- WRSMAT = .TRUE. (ensuring that the  $S$  matrices are written to the file jobname.smt).

The default value of {jobname} is the value you have set with the command JOB, or, if no value has been set, {jobname} = JOB

- **j1, in1**: rotational quantum number and additional index for the initial state
- **j2, in2**: rotational quantum number and additional index for the final state
- **ang1, ang2**: initial and final angle (in degrees)
- **dang**: step size (in degrees) in scanning through angles.
- **ienerg**: the cardinal value of the energy for which the differential cross section is computed. i.e. if **ienerg** = 2, then the second energy  $S$  matrices {jobname}2.smt are used
- **jtotend**: the maximum value of  $J_{\text{tot}}$  included in determining the scattering amplitude. The value of **jtotend** can not be larger than the variable JTOT2 used in the initial calculation
- **ipr**: If **ipr** = 0 (default) the degeneracy-averaged differential cross sections and product rotational alignment and hexadecapole moments are NOT printed to the normal output file but only to the file {jobnam}n.dcs. If **ipr**  $\neq$  0, the differential cross sections and the alignment ( $A_0^{(2)}$ ) and hexadecapole moments ( $A_0^{(4)}$ ) of the products are also printed to the normal output file and to stdout.
- **mflag**: If **mflag** = 0 (default) only the degeneracy-averaged differential cross section and the alignment ( $A_0^{(2)}$ ) and hexadecapole moments ( $A_0^{(4)}$ ) of the products are calculated. If **mflag**  $\neq$  0, then
  1. All  $m \rightarrow m'$  differential cross sections are calculated and printed. Quantization is in the collision frame, where the initial relative velocity vector defines the  $z$  axis.

2. The integral  $m \rightarrow m'$  cross sections are determined, by integration from `ang1` to `ang2` in steps of `dang`.
3. The diagonal ( $\rho_{m,m}$ ) and the real part of the 2<sup>nd</sup> supra-diagonal ( $\rho_{m,m+2}$ ) elements of the rotational density matrix of the scattered products are output into file `{jobnam}n.rho`. These quantities are defined here in terms of the scattering amplitudes.

- `stflag`: `stflag = 0` is the default. If `stflag  $\neq$  0`, then "heads" and "tails" steric cross sections are calculated (see [21]). This is only allowed if `flaghf = .TRUE.` and `ibasty = 3` (doublet pi). If `stflag  $\neq$  0`, then the following two parameters must be defined:
- `alpha, beta`: parameters which define the mixture of e and f  $\lambda$ -doublet states in the "heads" or "tails" orientation.

NB: the "heads" state for  $m$ -initial negative is defined as:

$$|\text{heads}\rangle = \alpha |jme\rangle - \beta |jmf\rangle \quad (31)$$

and for  $m$ -initial positive as

$$|\text{heads}\rangle = \alpha |jme\rangle + \beta |jmf\rangle. \quad (32)$$

### 6.3. Hyperfine-resolved integral cross sections: HYPXSC command

The command HYPXSC allows you to calculate hyperfine-resolved integral cross sections. These integral cross sections are printed in the terminal output and outputted to the file `jobnamen.hfx`, where `n` is the cardinal value of the energy (see below). The hyperfine-resolved cross sections are tabulated in columns as

$$E \ j_i \ I_i \ F_i \ j_f \ I_f \ F_f \ \sigma, \quad (33)$$

where `I` designates the nuclear spin.

The command line syntax is

`HYPXSC, {jobname}, ienerg, nucspin, j1min, j2max`

where `{jobname}`: the jobname under which the  $S$  matrices have been stored as `jobnamen.smt`. Here `n` denotes the value of the parameter `ienerg` (see below). The  $S$ -matrix files can be generated by setting the flag `WRSMAT = .TRUE.` The default value of `{jobname}` is set by the instruction `JOB = {jobname}` Note that for full close-coupling calculations it is necessary to carry out calculations for both values of the parity (this is ensured by setting `JLPAR = 0`; see the instructions for the `JLPAR` command for more information)

If no value of `{jobnam}` has been set, the default value of `{jobname}` is `Job`

- `ienerg`: The cardinal value of the energy for which the integral cross sections are to be computed. i. e. if `ienerg = 2`, then the second energy  $S$  matrix file `jobname2.smt` or second energy integral cross section file `jobname2.ics` are used. The default value of `ienerg` is 1
- `nucspin`: The value denoting the total nuclear spin  $I$  of the diatomic, `NUCSPIN=2*I` (0 for  $I = 0$ , 1 for  $I = \frac{1}{2}$ , 2 for  $I = 1$ , etc).
- `j1min`: Minimum value of the rotational angular momentum for which hyperfine cross sections will be calculated.
- `j2max`: Maximum value of the rotational angular momentum for which hyperfine cross sections will be calculated.

#### 6.4. Tensor cross sections: TENXSC command

The command TENXSC allows you to calculate the tensor cross sections defined by Eqs. (30) and (31) of Follmeg et al. [29]. The command line is

```
TENXSC, job, ienerg, iframe, lammax, kmax, in1, in2, jtotmx, jmin, jmax
```

where the input parameters are:

- `job, ienerg`: The program searches for an  $S$  matrix in the file `Jobienerg.smt`, where `ienerg` is an integer (`ienerg = 1, 2, ...` etc.) The default values of `job` is `JOB` and of `ienerg` is `1`.
- `iframe`: This parameter defines the quantization frame employed in the tensor cross section calculations (angle-integrated cross sections, except where indicated otherwise below).
- `iframe = 0`: The quantization axis is defined as the laboratory  $Z$ -axis, with an isotropic relative velocity distribution.
- `iframe = 1`: The quantization axis lies along the initial relative velocity vector (collision frame).
- `iframe = 2`: The initial level has quantization axis along the initial relative velocity vector, and the final level has quantization axis along the final velocity vector (helicity frame). In this case,  $m$ -resolved differential cross sections are computed over a grid of scattering angles (0.5 deg spacing) for the ( $J_{1MIN}, IN1$ )- $\rightarrow$ - $J_{1MIN}, IN1$ ) elastic transition, and then differential tensor cross sections are computed. The differential tensor cross sections are numerically integrated to determine integral tensor cross sections.
- `lammax`: The maximum value of the anisotropic term in the velocity distribution (lower case  $\lambda$  in the above article). Tensor cross sections for all even values of  $\lambda$  from 0 to `LAMMAX` are calculated. At present only `LAMMAX = 0` is operational!
- `kmax`: The maximum value of the multipole order for which tensor cross sections are calculated. Cross sections for all values of  $K_i$  and  $K_f$  .i.e. `KMAX` are calculated.
- `in1, in2`: The initial and final values of the additional index
- `jtotmx`: The maximum value included in the summation over total angular momentum (upper case  $J$  in Eqs. 30 and 31 of the above article)
- `jmin, jmax`: Tensor cross sections are computed for all values of the molecular rotational quantum number (lower case  $j_i$  and  $j_f$  in Eqs. 30 and 31 of the Follmeg et al. [29]) ranging from `jmin` to `jmax`.

To determine the  $S$ -matrix elements required by the command TENXSC, you must carry out a prior calculation with

- the flag `WRSMAT = .TRUE.`
- `jmin ... jmax` included in the array `JOUT`
- `in1` and `in2` included in the array `INDOUT`

## 7. Computational Considerations

Matrix operations (inversion, multiplication, solution of linear equations) impose the primary computational bottleneck to solution of the CC equations. Consequently, the total CPU time will be proportional to the operational count for this type of operation, namely  $N_{ch}^3$ ,  $N_{ch}$  being the number of channels (both open and closed) used. In practice, calculations are feasible for  $N_{ch}$  ranging up to several thousand, depending on the speed of the computer and the amount of memory available. The CPU time also depends linearly on the number of sectors (radial steps) required to integrate from  $R_{start}$  out to  $R_{end}$  (value of  $R$  such that the potential (exclusive of centrifugal barriers) becomes negligibly small). Typically, 5–10 sectors are necessary per deBroglie wavelength. As discussed in Sec. 2,

the hybrid (LOGD + AIRY) propagation scheme [9] makes use of a potential-following method at larger  $R$ , which allows a dramatic increase in sector width.

The determination of cross sections (and, subsequently, rate constants) requires integration of the coupled equations at many different values of the total angular momentum  $J$  and energy. This allows for straightforward parallelisation.

Hibridon can be run interactively, setting parameters in terminal mode and running short jobs. Alternatively, the program can be run in batch mode with a job script file. In either case, it is convenient to enter the parameters through an input file (\*.inp); an example of an input file is given in Appendix A.2.

## 8. Incorporating a PES

Hibridon is designed to be used as a library with a user-supplied PES. Notwithstanding, for test purposes and to help in incorporating a user's PES, several PESs are included in the Hibridon package. The coordinates used to describe the geometry of the PES of the collision complex should be appropriate for the calculation of matrix elements of the vibration-rotation scattering basis functions. Usually, only the radial coefficients of the expansion of the PES are required and should be carefully implemented in the code.

For each PES, the user is expected to provide three subroutines:

`loadpot`: Called only once, this subroutine's purpose is to initialize the PES data, possibly involving loading data from a file,

`pot`: Computes the radial coefficients for a given interparticle separation distance  $R$ ,

`driver`: this subroutine is used upon the summoning of the TESTPOT command and provides an interactive prompt that prints the value of the radial coefficients for a given interparticle separation distance  $R$ .

For the collision of Ar with  $N_2$ , examples of these three subroutines are given in Appendix A. Note that the simplistic Ar- $N_2$  PES used here is provided only as a template and is used only to benchmark the Hibridon code.

## 9. Distribution of the Code

The Hibridon package is fully available as a Github repository [44] under the GPLv3 license [84]. The compilation of the source files is cross-platform, compiler independent and automated using the CMAKE open-source software. Full instructions on how to build the Hibridon package can be found in the README.md file distributed along the source code. The proper building of Hibridon can be checked through automated testing using the CTEST tool from the CMAKE software. Those tests cover most of Hibridon's source code and ensure that a given installation behaves as intended. Each of these tests also represent fully working examples of PES implementations, input files, and expected output files that are accessible in the tests subfolder at the root of Hibridon's source code. A comprehensive user documentation, which extends and supplements the description given here, as well as adding more information and examples, is available as a wiki on Hibridon's Github repository webpage [44].

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## Appendix A. Example: the Ar–N<sub>2</sub> collisional system

The implementation of scattering calculations based on the Ar–N<sub>2</sub> PES of Pattengill et al. [85] is presented below. An sample input file and the resulting output file are also shown.

### Appendix A.1. Implementation of the PES

```

1 ! declare dummy subroutines syusr, bausr and ground. This is mandatory when the user does
   not provide his own basis (basis 99 and higher)
2 #include "common/syusr.F90"
3 #include "common/bausr.F90"
4 #include "common/ground.F90"
5
6 ! -----
7 ! subroutine called by testpot to interactively provide potential values
8 ! -----
9 subroutine driver
10 use mod_covvl, only: vvl
11 use mod_parpot, only: potnam=>pot_name
12 implicit none
13 integer :: ios
14 real(8) :: r, vv0
15 write(6, *) potnam
16 do while(.true.)
17     write(6,*) ' r (bohr)'
18     read (5, *, iostat=ios) r
19     if (ios /= 0) exit
20     call pot(vv0, r) ! values of the potential are returned in vv0 and vvl
21     write (6, "(' vsum', /, 7(1pe16.8))") vv0, vvl
22 end do
23 end subroutine driver
24
25 ! -----
26 ! subroutine to initialize the potential
27 ! -----
28 subroutine loopot(iunit, filnam)
29 use mod_parbas, only: ntv, ivcol, ivrow, lammin, lammax, mproj
30 use mod_parpot, only: potnam=>pot_name
31 implicit none
32 integer, intent(in) :: iunit ! if a data file is used, this subroutine is expected to
   use this unit to open it in read mode (not used here)
33 character*(*), intent(in) :: filnam ! if a data file is used, the file name of the
   data file (not used here)
34 integer, parameter :: l1i = 1 ! lambda1 index
35 potnam = 'PATTENGILL-LABUDDER-BERNSTEIN AR-N2'
36 lammin(l1i) = 2 ; lammax(l1i) = 2 ! lambda1's range is [2, 2]
37 mproj(l1i) = 0
38 ntv(l1i) = 1
39 ivcol(l1i, l1i) = 0 ; ivrow(l1i, l1i) = 0
40 return
41 end subroutine loopot
42
43 ! -----
44 ! calculates the r-dependent coefficients in the collision of Ar with N2
45 !
46 ! on return:
47 ! vv0
48 ! contains the isotropic term (n=0) in the potential.
49 ! vvl
50 ! the coefficients for each angular term in the coupling potential
51 ! [ vvl(i) for i = 1, nlam ] are returned in module mod_covvl
52 ! vvl(1) contains the anisotropic (n=2) term in the potential
53 ! -----
54 subroutine pot (vv0, r)

```



```

55 use mod_covvl, only: vv1
56 use mod_conlam, only: nlam
57 implicit none
58 real(8), intent(out) :: vv0
59 real(8), intent(in) :: r
60 real(8) :: eps, a6, a12, r0, eps_au, rat, w(6), rr0
61 data eps, a6, a12, r0 / 83.05d0, 0.13d0, 0.5d0, 3.929d0/ ! from reference paper above
62 w = (/ 1.0d0, 0.2d0, 0.1d0, 0.0d0, 0.025d0, 0.02d0/) ! weights
63
64 rr0 = r0 / 0.52917715d0 ! convert distance r0 to bohr
65 eps_au = eps / 219474.6d0 ! convert energy eps to hartree
66
67 rat = rr0 / r
68 vv0 = eps_au * (rat**12 - 2.d0 * rat**6)
69 vv1(1) = eps_au * (a12 * rat**12 - 2.d0 * a6 * rat**6)
70 vv1(1:nlam) = vv1(1) * w(1:nlam)
71 return
72 end subroutine pot

```

Listing 1. Example of PES implementation for the Ar–N<sub>2</sub> collisional system. This source file is used for testing purposes by Hibridon and can be found at hibridon/tests/arn2/pot\_arn2.F90.

### Appendix A.2. Input file

```

1  N2-Ar CC PATTENGILL POTENTIAL
2  1 ibasty
3  T T F F logdfl, airyfl, readpt, bastst
4  5.6000 8.0000 .1500 rstart, rendld, spac
5  F prairy
6  1.150 3.00 25.0 15.00 tolai, rincr, rendai, fstfac
7  1 nerg
8  500.0
9  16.47000 xmu
10 30.0000 rcut
11 20 20 5 1 0 0 1 jtot1,jtot2,jtotd,jlpar,numin,numax,nud
12 48 0 lscreen, iprint
13 4 1 nnout,niout
14 0 2 4 6
15 0
16 T T T F F prlogd, prsmat, prt2, t2test, wrsmat
17 F F F F F wrpart, prpart, prxsec, wrxsec, wavefl
18 F T F F F noprin, chlist, ipos, nucros, photof
19 F F F T F flaghf, csflag, flagsu, ihomo, twomol
20 F F rsflag, boundc
21 1 0 0 nvib, vmin,vmax
22 0 0 4 iv,jmin,jmax
23 2.01000 .000000E+00 .000000E+00 brot,drot,hrot
24 0.00000000 evib

```

Listing 2. Example input file for the Ar–N<sub>2</sub> collisional system. This input file is used for testing purposes by Hibridon and can be found at hibridon/tests/arn2/Arn2\_test.inp.

### Appendix A.3. Output file

```

1 Jan 20 15:31:43 2011
2 CC INTEGRAL AND PARTIAL TESTS
3 PATTENGILL-LABUDDÉ-BERNSTEIN AR-N2
4 500.000 16.470000000000
5 F F F F T
6 0 20 5 0 0 1 1 0
7 6 6
8 0 0 2 0 4 0 6 0 8 0 10 0
9 0.00000000E+00 5.49494110E-05 1.83164703E-04 3.84645877E-04 6.59392932E-04 1.00740587E-03
10 2.67327978E+00 1.15913251E-01 1.31726776E-02 7.07522265E-02 8.64761274E-02 1.64014777E-02
11 5.65587118E-01 1.60330543E+00 2.20464398E-01 1.59154052E-01 2.17193851E-01 6.60399047E-02
12 1.09022349E-01 3.73949982E-01 2.06368973E+00 3.14756214E-01 2.98168618E-01 1.57533017E-01

```

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13 7.64483467E-01 3.52435191E-01 4.10923357E-01 2.16095716E+00 3.25244646E-01 2.92131612E-01
14 1.04459011E+00 5.37688541E-01 4.35181213E-01 3.63606675E-01 2.60890434E+00 5.37612771E-01
15 1.92123630E-01 1.58539623E-01 2.22960496E-01 3.16700226E-01 5.21335986E-01 4.04890105E+00

```

Listing 3. Output file for the Ar–N<sub>2</sub> collisional system. This output file is used for testing purposes by Hibridon and can be found at [hibridon/tests/arn2/Cctest1.ics](https://hibridon.com/tests/arn2/Cctest1.ics).

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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